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THE EFFECT OF ENVIRONMENT ON THE CORROSION OF METALS
IN SEA WATER--A LITERATURE SURVEY

by

Howard A. Porte, Ph. D.

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NAVAL CIVIL ENGINEERING LABORATORY
Port Hueneme, California

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ABSTRACT

The U. S. Naval Facilities Engineering Command is interested in developing methods to combat metallic corrosion as a means of reducing maintenance costs of the Naval Shore Establishment.

A literature survey was made to determine the effect of environmental variables on the corrosion rates of metals submerged in sea water. The most important variables were found to be dissolved oxygen concentration, velocity, and temperature. Other factors which influence the corrosion rates are pH, salinity, and micro-organisms. It is recommended that a coordinated research program, consisting of basic research studies and corrosion testing, be initiated in controlled sea water environments.

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INTRODUCTION

This report is the first phase of a research program intended to investigate the effects of physical, chemical, and possibly biological factors present in natural environments on the deterioration of metals, particularly mild steel. Such a study will provide knowledge that can lead to improved techniques for protection of metals against the degrading effects of different natural environments.

The Appendix presents an outline of a very broad program, within which practically any research and evaluation study on the deterioration effects of natural environments on materials can be placed. It is included to show the reader the part this particular literature survey and its logical extension to new laboratory research in areas not yet covered, can play in the total picture of material deterioration.

This literature survey is concerned with the corrosion of metals and alloys submerged in sea water which is, of course, a very corrosive solution. Historically, the corrosion of materials in the marine environment has been of great importance. It is not surprising that many studies have been made to evaluate the performance of metals and alloys in various marine environments. The results of these studies have been summarized in a number of technical publications.¹⁻⁷

It may be predicted that as man accelerates his exploitation of the natural resources found beneath the surface of the oceans there will be increasing needs for economical corrosion resistant materials. Designers of marine equipment are primarily interested in the cost and expected service life of materials for particular applications. However, in spite of the large amount of corrosion information, in many situations it is difficult to choose the most economical material because quantitative corrosion rate data vary over wide ranges.

Carbon and low-alloy steels are the basic materials of construction for marine structures and ships. The corrosion rate of scale-free mild steel in aerated, unpolluted sea water is reported⁸ to average about 25 mg per sq decimeter per day (mdd) but corrosion rates as low as 5 mdd⁹ and as high as 2040 mdd¹⁰ have been observed. Obviously, certain changes in the sea water environment must be responsible for these large differences in corrosion rates. It was the object of this literature survey to find out what is known about the effects of chemical, physical and biological variations in the sea water environment on the corrosion rates of metals. The literature was searched for those studies where corrosion rates were measured as a function of one or more environmental variables in natural sea water, artificial sea water, and neutral solutions.

THE SEA WATER ENVIRONMENT

Sea water is an extremely complex, heterogeneous solution. It contains a large amount and diversity of dissolved solid material, dissolved gases, and various species of biological matter. Reaction equilibria and the mechanisms by which materials corrode in sea water are not clearly understood. The most important sea water parameters, from the corrosion standpoint, are salinity, pH, dissolved oxygen concentration, temperature, velocity and types of biological species. A typical analysis of the major constituents of sea water¹¹ is given in Table 1.

Table 1. Major Constituents of Sea Water¹¹

Ion		ppt
<u>Anion</u>		
Chloride, Cl ⁻	18.9799
Sulphate, SO ₄ ⁻	2.6486
Biocarbonate, HCO ₃ ⁻	0.1397
Bromide, Br ⁻	0.0646
Flouride, F ⁻	0.0013
Boric acid, H ₃ BO ₃	0.0260
<u>Cation</u>		
Sodium, Na ⁺	10.5561
Magnesium, Mg ⁺⁺	1.2720
Calcium, Ca ⁺⁺	0.4001
Potassium, K ⁺	0.3800
Strontium, Sr ⁺⁺	0.0133

Salinity is defined as the weight in grams of dissolved inorganic matter in 1 kilogram of sea water, after all bromide and iodide has been replaced by chloride, all carbonate converted to oxide, and all organic matter completely oxidized. The salinity of natural ocean water is about 34 parts per thousand (ppt) but may vary between 32 to 37 ppt at different locations and depths.

The change in salinity with depth at one location in the Pacific ocean off the coast of California¹² is shown in Figure 1.

The temperature of sea water tends to approach air temperature at the ocean surface which means that it varies with geographical location and also with ocean currents. As depth increases the temperature of sea water decreases approaching 0°C at the lowest depths. The change of temperature with depth at one location is shown in Figure 1.

The pH of sea water in equilibrium with air is about 8.2 but may range from 7.2 to 8.6; at one location it changed with depth as indicated in Figure 2. In general, a pH maximum (8.2 to 8.3) exists near the surface, within the first 100 meters. This pH maximum exists as a result of the water temperature, the air-sea carbon dioxide exchange, and biological activity. The pH then decreases to a minimum at a depth range at 200 to 1200 meters after which an increasing trend with depth is observed.

The quantity of oxygen in air-saturated sea water at the ocean surface is normally about 6 ml/liter but is dependent upon temperature and salinity and changes with depth as shown for one location in Figure 2. Behaving in a manner analogous to pH, dissolved oxygen concentration has a maximum value at or near the surface. It decreases to a minimum in the range of 200 to 1000 meters and then shows an increasing trend with depth.

The velocity of sea water and the concentration and species of biological matter may also be considered as important parameters for the corrosion of metals. The velocity may vary from essentially stagnant conditions to currents of 1 or 2 meters per second. The type of biological species vary with geographical location, of course, and in general tend to be in higher concentration near the water surface than at great depths. It has been

stated¹⁴ that "natural seawater differs from synthetic seawater, from the corrosion standpoint, mainly because of the effects of the living organisms present in the ocean". Because of the complexity of natural sea water, there has been a tendency of many workers to carry out investigations in more convenient environments, such as sodium chloride solutions. However, it has been shown in many cases^{15,16} that the results obtained in sodium chloride solutions are not the same as in the more complex natural sea water. LaQue¹⁷ recommends that where it is not possible or very inconvenient to use natural sea water for laboratory investigations, a synthetic seawater, such as the mixture adapted by the American Society for Testing Materials,¹⁸ is preferable to sodium chloride solutions.

EFFECTS OF ENVIRONMENTAL VARIABLES ON CORROSION RATES

Dissolved Oxygen

The corrosion of metals in an aqueous solution is known to be an electrochemical process. This means that (a) the corrosion reaction can be divided into an oxidation and a reduction reaction both involving the transfer of electrons and (b) there are conducting ions in the solution. If iron is the metal under consideration, the oxidation reaction, which takes place at anodic areas of the metal, is: $\text{Fe} = \text{Fe}^{++} + 2e$. The reduction reaction, which takes place at cathodic areas of the metal, in deaerated (oxygen-free) solutions is: $2\text{H}^+ + 2e = \text{H}_2$. The overall reaction is the sum of the anodic and cathodic reactions. From a thermodynamic point of view this reaction can and will take place. However, the rate at which this reaction takes place is determined by the kinetics of the system. This means that the rate of the overall corrosion process is controlled by the slowest step which in this case is the reduction reaction. In deaerated neutral or near neutral (pH 4 to pH 9) solutions at room temperature, the rate of the reduction step is very slow due to the low concentration of hydrogen ions and therefore the corrosion rate of iron and steel is negligible.

When dissolved oxygen is present, the reduction reaction which takes place on cathodic areas of the metal becomes: $2\text{H}^+ + 1/2 \text{O}_2 + 2e = \text{H}_2\text{O}$. This reaction proceeds at an appreciably faster rate than the one above where no oxygen was present. However, in order for the dissolved oxygen to react it must reach the metal surface and this is accomplished by diffusion through the solution. Thus the corrosion rate is limited by the rate of diffusion of dissolved oxygen. Since the diffusion rate is proportional to the dissolved oxygen concentration it follows that the corrosion rate is also proportional to the dissolved oxygen concentration.

Uhlig, Triadis, and Stern¹⁹ studied the effect of oxygen concentration on the corrosion of mild steel in slowly moving distilled water and in water containing 165 ppm calcium chloride, at 25°C. For the calcium chloride solution, the corrosion rate was found to be a linear function of dissolved oxygen concentration in the range 0 to 6 ml oxygen/liter (air-saturated water). For distilled water the corrosion rates were also found to increase with

dissolved oxygen concentration although the corrosion rates were somewhat lower than in the calcium chloride solutions. In the absence of dissolved oxygen corrosion rates were negligible in both solutions.

Frese²⁰ studied the effect of oxygen concentration on the corrosion rates of mild steel and stainless steel in a 3-½ percent sodium chloride solution. By varying the oxygen pressure in a reaction bomb, corrosion rates were determined above, below, and at the oxygen concentration found in an air-saturated solution. The results are listed in Table 2. For mild steel the corrosion rates increase steadily with increasing oxygen pressure indicating that no protective film was formed. In contrast stainless steel showed a maximum corrosion rate at 0.2 atmosphere oxygen pressure (air-saturated solution). This result was explained by the assumption that at elevated pressures a more adherent and protective film was formed on stainless steel.

Table 2. Effect of Oxygen Pressure on the Corrosion Rate of Stainless Steel and Mild Steel in 3.5% NaCl Solution at Room Temperature²⁰

Oxygen Pressure (atmos.)	Corrosion Rate, mg/dm ² /day	
	Stainless Steel	Mild Steel
0.0	0.0	0.71
0.2	0.2	11.8
1.0	0.02	51.2
9.66	0.0	470
61.3	0.02	1,640

In the corrosion of mild steel in distilled water, Uhlig¹⁹ et al also observed a decrease in corrosion rates at high oxygen pressure. This decrease in corrosion rate was caused by the passivation of iron at higher oxygen pressures. This behavior is not possible, of course, in sea water or solutions where appreciable concentrations of chloride are present because passivity of iron cannot be established in such media. The effect of increased oxygen concentration on the corrosion rate of mild steel in salt water is shown qualitatively in Figure 3.

Hydrogen Ion Concentration

The effect of pH on the corrosion of iron in aerated water at 22°C was studied by Whitman, Russell, and Altieri.²¹ They found that the corrosion rate was essentially the same in the pH range 4-10, as shown in Figure 4. Below pH 4, in the acid region, corrosion rate increases rapidly with hydrogen evolution. Above pH 10, in the alkaline region, the corrosion rate decreases. Since the pH of sea water is about 8 it would be expected that small variations in the pH of sea water would not have a marked effect on the corrosion rate of iron at room temperature.

Above room temperature, at 40°C, the corrosion rate was found to be independent of pH in a narrower range, pH 5 to pH 8.

With amphoteric metals, such as aluminum, lead, and zinc, the oxide film is only protective in the neutral or near neutral pH ranges at room temperature. In either strong acids or strong alkaline solutions the oxide is soluble resulting in severe attack. The pH range where corrosion rates are low for aluminum²² is between pH 4.5 to 8.5; for zinc,²³ pH 7 to 12.5; for lead,²⁴ pH 3 to 11. These "safe" pH ranges will vary from metal to metal and also are dependent on temperature.

Temperature

For most chemical reactions, the reaction rate increases with increasing temperature. Temperature affects the corrosion rate of metals in electrolytes primarily through its effect on factors which control the diffusion rate of oxygen.²⁵ The corrosion of iron and steel is an example of this because temperature affects the corrosion rate by virtue of its effect on the oxygen solubility and oxygen diffusion coefficient. As temperature increases the diffusion coefficient of oxygen also increases which tends to increase the corrosion rate. However as temperature is increased oxygen solubility in aqueous solutions decreases until at the boiling point all oxygen is removed; this factor tends to decrease the corrosion rate. The net effect for mild steel,²⁶ illustrated in Figure 5, is that the corrosion rate approximately doubles for a temperature rise of 30°C up to a maximum temperature at about 80°C, the rate then falls off in an open system because the decrease in oxygen solubility becomes the most important factor. In a closed system, where oxygen cannot escape the corrosion rate continues to increase indefinitely with temperature until all the oxygen is consumed.

The corrosion rate of Admiralty brass and cupro-nickel doubles for a 20° rise in temperature in the temperature range 0 to 75°C in three percent sodium chloride.²⁸ The rate of pitting of stainless steel in chloride solutions also increases with increasing temperature,²⁸

Temperature can also affect the corrosion rate by changing the nature of the corrosion film. This was demonstrated by Cox²⁹ in a study of the corrosion of zinc in distilled water. At room temperature the corrosion product is gelatinous and adherent but at about 50°C the film becomes granular and non-adherent. A maximum corrosion rate is reached at about 65°C after which the rate decreases again due to decreased oxygen solubility and the formation of a compact, dense and adherent film.

The effect of temperature on the corrosion rate of metals in sea water is thus seen to be quite complicated. Changes in temperature affect the chemical composition and physical properties of sea water, the nature and properties of corrosion products, the electrochemical behavior of metals themselves, and of particular interest the solubility and diffusion rate of dissolved oxygen.

Velocity

In general, any increase in the relative motion between a metal and the corrosive solution will accelerate the corrosion. The most important consequences of increasing the velocity are (1) an increase in the transport of dissolved oxygen to the metal surface and (2) disturbance of the adherent properties of the corrosion film. In some situations, motion may cause local attack. In other cases, motion may eliminate local attack. A general review of the effect of velocity on corrosion by water was made by Copson³⁰ of work done prior to 1952 for iron, zinc, copper, and their alloys.

In all real systems some motion will always be present. Even in the case of so-called "stagnant" conditions there is some motion due to natural convection. The motion is markedly increased where forced convection is present, such as water flowing through a pipe or a ship moving through the water.

For diffusion controlled reactions the relationship between the corrosion rate, R , and the velocity, V , of the liquid is of the form: $R = k_1 C^{5/4} + k_2 C V^n$ where C is the bulk concentration of dissolved oxygen in the solution, and where k_1 , k_2 , and n are constants. The first term may be regarded as the contribution of natural convection which becomes negligible at high flow rates. The equation then reduces to: $R = k_2 C V^n$. The value of n is in the range from 1/3 to 1; it depends on (a) the type of flow, which may be either laminar or turbulent depending on the Reynolds number for a particular system, and (b) the geometry of the metal surface. Under laminar flow conditions for water flow in a pipe n is 1/3, while for a plate placed in a current of water parallel to the direction of flow, n is one-half. Under turbulent conditions the value of n will increase. It is apparent that velocity and flow patterns can be major factors in the corrosion of metals by water. Several sources^{31,32,33} treat these hydrodynamic considerations in further detail.

In practice it is often found that the corrosion rate initially increases with increasing velocity but that at very high velocities the corrosion rate becomes relatively independent of velocity. This indicates that the corrosion rate was initially diffusion controlled but at very high velocities became activation controlled. This general type of behavior, illustrated in Figure 6, is characteristic of steel and copper based materials. It was observed

by LaQue³⁴ in a study of the effect of velocity on the corrosion of steel in sea water at atmospheric temperatures and by Speller and Kendall³⁵ in an investigation of velocity on the corrosion of half-inch steel pipe in oxygenated water (Pittsburgh City water) in the velocity range 0.03 to 2.4 m/sec.

Certain materials, such as stainless steels and many nickel base alloys, which depend on a good supply of oxygen to maintain the integrity of the passive film actually perform better at high velocities. In stagnant sea water these materials form deep pits but at continuous high velocities give low (less than 5 mdd) corrosion rates and have less tendency to pit.⁶

Some interesting results were obtained in a study³⁶ of the effect of velocity of sea water flow on the corrosion of some steels and cast irons. Low alloy steel was found to corrode as fast as plain carbon steel when the velocity was under 12 m/sec, but at 16 m/sec. it developed better corrosion resistance than plain carbon steel. Corrosion of the cast iron was practically the same for different flow velocities.

In a recent study³⁷ of the corrosion of copper, copper alloys, and carbon steel in flowing 3% sodium chloride solution it was concluded that the corrosion rates were mainly determined by mass-transfer phenomena. In the case of carbon steel, the supply of oxygen to the metal surface determined the corrosion rate. In the case of copper and its alloys, on the other hand, the corrosion rates were limited by the removal of corrosion products from the metal surface and thus the supply of oxygen was not rate-determining. For all metals investigated, a marked increase in the corrosion rate was observed at the transition from laminar to turbulent flow. The corrosion rates for carbon steel ranged from 71 mdd at a velocity of 0.0001 m/sec to 930 mdd at 7.3 m/sec.; for copper the corrosion rates ranged from 30 mdd at 0.0001 m/sec. to 125 mdd at 7.3 m/sec.

In a study³⁸ of the corrosion of a number of steels, and copper, aluminum, and magnesium alloys in flowing synthetic sea water, all materials showed a higher corrosion rate as water speed was increased from 2 to 16 m/sec. The corrosion rates at two to 16 m/sec. were found to be 65 to 530 mdd for carbon and low alloy steels, 1.3 to 3.1 mdd for stainless steel, 6.4 to 21 mdd for aluminum-bronze, and 6.9 to 60 mdd for brass.

A study³⁹ has been made on the effects of flow rates ranging from 0 to 5 meters per second on the galvanic corrosion of low-carbon steels in sea water at 0°C. The corrosion of the steels forming galvanic cells was found to be up to 15 times as great at high rates of flow as in standing sea water. Potential measurements revealed that the variation of the flow rate did not alter the order of nobility of the examined steel. It was seen that the higher the silicon content of the steel, the less noble is its potential. Galvanic corrosion can be particularly serious in the welded seams of ships, where the weld metal is strongly anodic to the ship plate.

Dissolved Salts

The effect of dissolved salts on the corrosion of steel in aerated water is shown qualitatively in Figure 7.⁴⁰ It was observed that the

corrosion rate initially increases, reaches a maximum, and then decreases with increasing salt concentration. For sodium chloride, Borgmann⁴¹ showed that for mild steel the maximum occurred at about 0.5 N (3% NaCl); coincidentally, this is the same concentration of sodium chloride found in sea water. Potassium chloride solutions were found to be more corrosive than sodium chloride with a maximum corrosion rate occurring at 0.5 N and lithium chloride solutions were found to be less corrosive with a maximum corrosion rate occurring at 0.25 N. Thus it may be concluded that in chloride solutions the corrosion rate of steel is dependent on both the concentration of anion and the type of cation.

The corrosion of zinc in aerated aqueous solution also shows a dependence on salt concentration. In a study⁴² at 25°C the corrosion was determined for solutions containing 0, 30, 90 and 200 g/l sodium chloride. The corrosion rate showed a maximum at 90 g/l sodium chloride.

The total salt content (salinity) of seawater may show variation with geography, depth, and temperature. If these variations were appreciable, they would have considerable effect on the corrosion rate of metals. However, if the average salinity of seawater is considered to be about 34 ppt,¹¹ and if the variations in salinity are in the range from 32 to 36 ppt then the effect on corrosion rate would be relatively small, perhaps a few percent. Thus in the natural seawater environment, the normally small variations encountered in seawater salinity and in the relative proportions of dissolved salts should exert a minor effect on the corrosion rates of metals.

Micro-Organisms

Although a large number and variety of organisms exist in sea water, the most important micro-organisms in their effects on corrosion rates are the sulfate-reducing bacteria (Desulphovibrio desulphuricans). The role of sulfate-reducing bacteria in the anaerobic corrosion of iron and steel was first described by von Wolzogen Kuhr and van der Vlugt.⁴³ These bacteria are most prevalent in an anaerobic (oxygen-free) environment where the pH value is between 5.5 and 8.5. The general effect is to reduce sulfates, and produce hydrogen sulfide on the iron surface. The mechanism is still somewhat in controversy. It was originally⁴³ postulated that the corrosion is stimulated by the removal of hydrogen from cathodic areas of the metal surface however an alternative mechanism proposes⁴⁴ that the action of the bacteria is simply to stimulate the anodic process through the production of sulfide.

A recent study⁴⁵ examines the effect of different strains of sulfate-reducing bacteria on the corrosion of mild steel. Several fresh water strains (D. desulphuricans) and three salt water strains (D. desulphuricans var. aestuarii) were studied. The results are shown in Table 3. For the fresh water strains, a very good linear correlation between the rate of corrosion and the hydrogen adsorption coefficients of the bacteria strains was obtained. The results obtained with the salt water strains however, did not fit well into the pattern shown by the fresh-water strains. One of the salt water strains (California 43:63) showed a very high corrosion rate and had the

Table 3. Effect of Different Sulphate-reducing Bacteria Strains on the Corrosion of Mild Steel⁴⁵

System	Mean Rate of Corrosion, $\text{mg/dm}^2/\text{day}$
FRESH WATER	
Sterile	1.4
D. desulphuricans	
Llanelly	6.6
Hildenborough	5.6
Teddington R.	3.9
America	3.4
Benghazi	3.0
D. orientis	
Singapore	2.6
SALT WATER	
Sterile	1.4
D. desulphuricans; var.	
aestuarii	
California 43:63	6.6
El Agheila C	4.8
El Agheila Z	3.8

Table 4. Effect of Periodic Cleaning on the Corrosion Rate of Steel Immersed in Sea Water⁵²

Steel	Corrosion Rate, * $\text{mg/dm}^2/\text{day}$	
	Cleaned Monthly	Cleaned After 1 Year
Carbon Steel	48	22
Ship Plate	50	21
2.7 Ni Steel	48	21

* Based on a one year exposure.

lowest value for the hydrogen absorption coefficient. One of the conclusions of the authors was that "it is clear that the fundamental biochemistry of the sulfate-reducers requires more intensive study".

Other iron-corroding micro-organisms include⁴⁶ sulfur-oxidizing bacteria (Thiobacillus thiooxidans), iron- and manganese-precipitating bacteria (Gallionella ferruginea), hydrogen-fixing bacteria (Hydrogenomonas flava), and film-forming bacteria. There is also some evidence for nitrate- and methane reducing bacteria.

Although much work^{47,48,49} has been done on the biological involvement in metal corrosion many questions remain unanswered and it is obvious that much further work is necessary before a satisfactory unified theory relating biology with corrosion will be available.

Corrosion Deposits

In many systems it is observed that the corrosion rate decreases with time due to the build-up of corrosion products on the metal surface. In the iron/water system the accumulation of hydrated iron oxide (rust) on the surface restricts the diffusion of oxygen from the bulk solution to the metal interface. In a study⁵⁰ of the corrosion of mild-steel tubes through which chloride solution was flowing the corrosion/time curve was represented by an equation of the form: $W = k_1 t / (1 + k_2 t)$, where k_1 is the initial corrosion rate and k_2 is a "blocking factor" describing the retardation in corrosion rate, W is the weight gained, and t is the time. The corrosion product consisted of a mixture of magnetite, Fe_3O_4 , and hydrated ferric oxide, the latter being the major constituent in outer layers. The hydrated oxide was mainly gamma- $FeOOH$ with small amounts of alpha- $FeOOH$ and alpha- Fe_2O_3 . From bulk density determinations the product was found to be spongy in character with voids occupying 50% of the total volume.

Usually, when thick continuous corrosion films are formed the overall corrosion rate is decreased; however, films that are non-uniform or discontinuous tend to set up concentration cells which can result in severe pitting.

On the basis of many tests of steel immersed in sea water it seems well established that specimens which are periodically cleaned lose more weight but are less deeply pitted than specimens which are left undisturbed. In continually immersed tests in seawater⁵¹ it was found that cleaned steels lost more in weight and were less deeply pitted than steels with a scale. Another series of tests⁵² showed that steel specimens immersed in sea water which were cleaned monthly had a corrosion rate more than twice as fast as steel which was left undisturbed for one year, as indicated in table 4.

CONCLUSIONS AND RECOMMENDATIONS

1. Although sea water is an extremely complex solution which defies exact analysis, the variation of certain parameters has been shown to produce important effects in the corrosion of metals and alloys.

2. The most important factors which affect the corrosion of metals immersed in unpolluted sea water are dissolved oxygen, velocity, and temperature. For low carbon steel in sea water saturated with air, i.e., with dissolved oxygen concentration of 6 ml/l, the following range of corrosion rates might be expected: from 25 mdd to 125 mdd at 25C and velocities from 0 to 2 m/s; from 15 mdd to 75 mdd at 1C and velocities from 0 to 2 m/s. In the absence of dissolved oxygen, negligible corrosion rates can be expected between 1 to 25C. In general, the rate of attack is increased with (a) larger concentration of dissolved oxygen, (b) higher sea water velocities, (c) raising the temperature.

3. Other factors which influence the corrosion of metals in sea water are pH, salinity, and micro-organisms. For iron and steel, the corrosion rate increases as the pH is lowered (becomes more acid); for amphoteric metals such as aluminum and zinc, increased attack is observed as pH changes from neutral solutions in both acid and alkaline directions. For most metals the corrosion rate increases as the salinity increases up to a maximum at a particular salt concentration after which the corrosion rate decreases with increasing salinity. The presence of sulfate-reducing bacteria increases the corrosion rate.

4. It is recommended that a coordinated research program be conducted to investigate the behavior of carbon steel, high strength steels, copper, aluminum, titanium, and selected alloys in natural sea water.

This program should consist of two parts:

a. A basic research program to investigate the mechanism of corrosion of metals in sea water. The environment would be controlled so that the individual corrosion effect of dissolved oxygen, velocity, temperature, pH, salinity, and bacteria, could be established for each metal and alloy. The objective of this research would be to indicate the range of usefulness for each variable. This would serve as a guide in the selection of the proper material for a specific application.

b. A corrosion testing program to obtain corrosion rate data for metals in controlled sea water environments. The environmental factors should be controlled to simulate service conditions. An objective of this program would be to obtain the necessary data to assist designers in (a) allowing for suitable corrosion, and (b) providing for corrosion control.

ACKNOWLEDGMENT

Mr. C. W. Mathews assisted in searching the literature and obtaining reference material.

APPENDIX

OUTLINE OF AN APPROACH TO A LONG RANGE RESEARCH, DEVELOPMENT AND EVALUATION PROGRAM ON PREVENTION OF DETERIORATION OF MATERIALS OF CONSTRUCTION

by

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ABSTRACT

The deterioration of materials of construction has a severe economic impact on world-wide activities, including those of the Naval Facilities Engineering Command, U. S. Navy. An outline of very broad scope is presented with intent to point up the tremendous need and opportunity for research in this area of effort. In addition to listing materials of concern, emphasis is given in the outline to: the importance of different sorts of environmental parameters influencing deterioration; the need for more information about the mechanics and mechanisms of deterioration; and, the need for more research and evaluational studies concerned with methods to control or prevent deterioration.

INTRODUCTION

Practically all materials of construction undergo degradation or deterioration in a natural environment. Control or prevention of such damage can be a discouraging and complex problem. Maintenance and repair, or replacement, of materials that have undergone severe deterioration is a matter of great concern to the Naval Facilities Engineering Command, U. S. Navy, in the fulfillment of its mission to construct, maintain and operate the Naval Shore Establishment that exist throughout the world. Were there no material deterioration, only a small fraction of the manpower and funding now used would be required by these field activities. Thus, even small progress toward reduction of maintenance problems resulting from materials deterioration would have significant impact on the Command's fiscal needs.

Ironically, if baser metals and alloys did not rust and tend to return to an oxidized form, in which they were found in nature, if wood and other cellulosic materials were not subject to attack by termites, beetles, marine borers, etc., if plastics were not degraded by atmospheric exposure and had all the structural strength desired, and if coatings remained unaffected by weather and marine environments, including fouling, the economy of the world--and particularly of the United States--would be

affected profoundly. Structural and decorative materials, once fabricated, would not have to be replaced or repaired, and international requirements for them would be drastically reduced. Such an idealized situation is so far from realistic fulfillment in the near future that possible deterring considerations such as these need not be considered. A reduction of deterioration effects, as great and as rapidly as possible, is of prime importance.

Since its inception as the research and development agency of the Naval Facilities Engineering Command, the U. S. Naval Civil Engineering Laboratory has been investigating construction problems closely related to Command responsibilities and requirements. Among its major concerns are the selection of proper materials for construction projects and for the maintenance of structures already fabricated. The subject of construction materials and their deterioration is very broad, cutting across many lines of responsibility delegated within the Laboratory as well as in the various Naval Shore Establishments.

This note presents an outline in very brief, skeletal form to encompass those broad areas concerned with the problem of material deterioration. It is meant to be quite comprehensive--no one research agency is likely to have the capability to investigate all of the outline areas simultaneously.

DISCUSSION

A glance at the types of materials (Item I) included in the outline is evidence of the broad scope which it covers. The deterioration (Item III) of each of these materials involves distinctly separate problems, except for occasional overlaps illustrated, for example, by the extent to which corrosion of reinforcing bars may cause reinforced concrete to spall.

The outline emphasizes the role played by widely different environmental factors (Item II) in material deterioration. Much more information must be obtained if these factors are to be properly related to the results of actual exposure. The synergisms reinforcing one another in different environments must be discovered and studied for methods of control. Each type of control (Item IV) is a basis for considerable research and evaluation effort in both laboratory and field, and each has been, is, or could be the subject of a considerable development program.

The fact that research programs are presented as subheadings in the outline must not be interpreted as an effort to downgrade the contribution to be made by research. On the contrary, only through research can we expect to learn more about the basic causes of deterioration and how they operate. Once all such information is known through research, the development of new, improved methods of control can be extended beyond the empirical trial-and-error procedures that have marked much of the earlier efforts in this field.

This outline was prepared, and is intended to serve, as a guideline to those at the U. S. Naval Civil Engineering Laboratory who are interested and participating in the different facets of the tremendous problem areas which it represents. It can be used to illustrate that only a small part of the total unknown in the Materials Deterioration field is currently

under investigation at this Laboratory. Moreover, it can also contribute to a more coherent program by providing a straight-forward presentation of factors that are interrelated and by making it easier to select from the total, those that need higher priority treatment. Specific task instructions can be fitted into their proper place in the outline, and new project proposals can be prepared with a view to rounding our definite parts of the outline where gaps in present knowledge exist.

OUTLINE

In scope, this outline is intended to cover research and evaluation investigations of materials in standard and generally accepted uses and environments, and in new materials applications.

In addition to the four main headings presented, a fifth is included to call attention to other problem areas that demand effort and attention. However, from a research viewpoint, these are not comparable in scope to the problem areas covered under the first four headings.

I. Types of materials to be investigated:

- A. Metals, including alloys
- B. Concrete
- C. Polymers, including plastics and ceramics
- D. Natural materials, including fibers and cellulosic materials
- E. Others

II. Environments

A. Types of environment

1. Atmospheric, including coastal or island, inland, structural interiors
2. Marine, including intertidal and surface, subsurface, deep ocean, ocean floor
3. Other liquids
4. Subsoil
5. Others

B. Physical Factors, as appropriate

1. Temperature
2. Moisture content
3. Precipitation
4. Cyclic changes, such as heating and cooling, wetting and drying, and freezing and thawing
5. Electromagnetic radiation, including ultraviolet, visible, and infrared
6. Wind
7. Electrical conductance
8. Abrasive factors
9. Current and tidal actions
10. Others

C. Chemical Factors, as appropriate

1. Salt spray
2. Impurities and pollution
3. Different anions and cations present, and pH
4. Oxygen content
5. Moisture
6. Incompatibility of materials that interact
7. Others

D. Biological Factors

- a. Types of attacking organisms
 - (1) Microorganisms

- (a) Enzymatic attack
- (b) Release of deterioration-causing products
- (c) Relationship to other attacking organisms and attack mechanisms (synergisms)
- (2) Fouling organisms
 - (a) through (c), as above
 - (d) Mechanical attack
- (3) Boring and chewing organisms
 - (a) through (d), as for (2), above
- (4) Others
- b. Mechanisms or mechanics of attack
- c. Deterioration of Ecology of attacking organisms

III. Deterioration of Materials

- A. Research on mechanics or mechanisms of deterioration
- B. Studies of deterioration in above environments, including statistical treatments
 - 1. Studies of cause-and-effect interrelations between deterioration and environment

IV. Control or Prevention of Deterioration

- A. Types of control, as appropriate
 - 1. Protective coatings and paints
 - 2. Thin protective films, their hardness, permanence and adhesion
 - 3. Corrosion inhibitors
 - 4. Lubricants

5. Cathodic protection
 6. Toxic and fire retardant impregnants
 7. Sheathing and barriers
 8. Sealers
 9. Modifiers for plastics such as ultraviolet absorbers, fillers and plasticizers
 10. Others
- B. Research on mechanics or mechanisms of protective methods
 - C. Studies on protective methods
- V. Other Problem Areas
- A. Installation and maintenance procedures
 - B. Special cases
 1. Airfield marking paints
 2. Jet blast damage
 3. Boiler scale and other water residues
 4. Others

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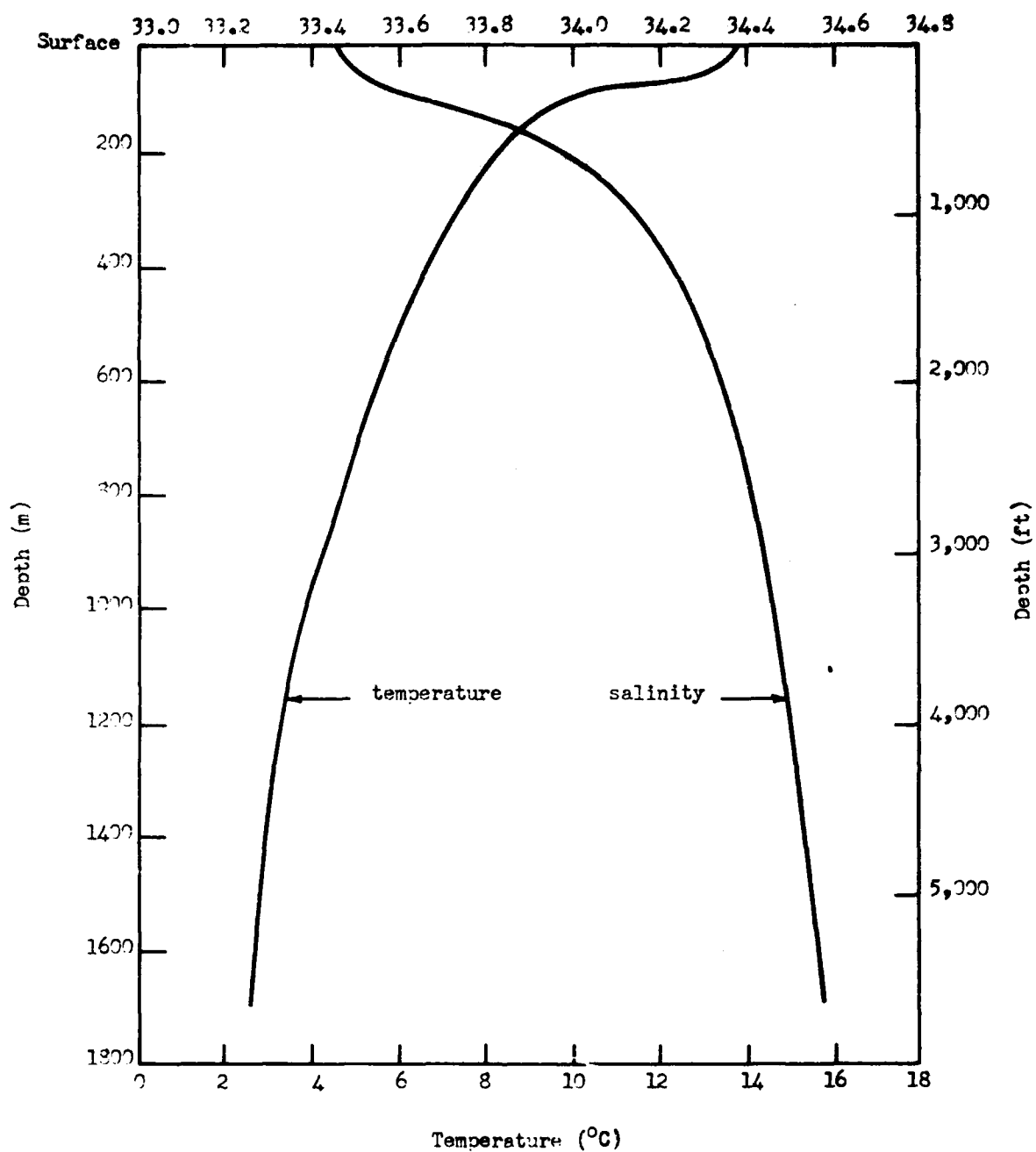


Figure 1. Variation of Salinity and Temperature with Depth¹²

Location: Pacific Ocean; 34°N , 121°W .

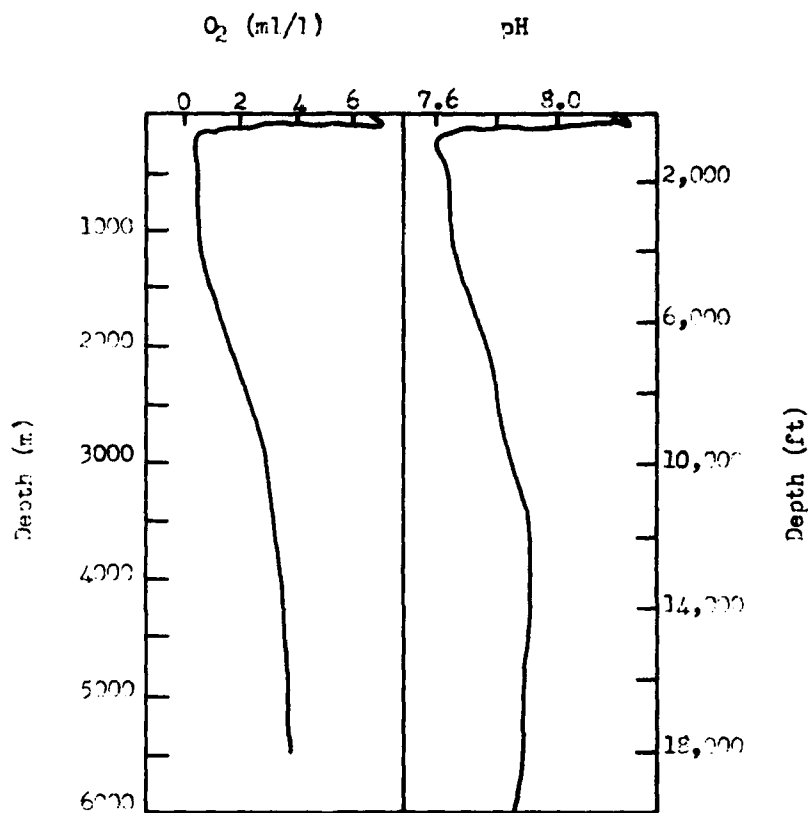


Figure 2. Variation of pH and Dissolved Oxygen with Depth¹³
Location: Pacific Ocean; 54°N, 159°W.

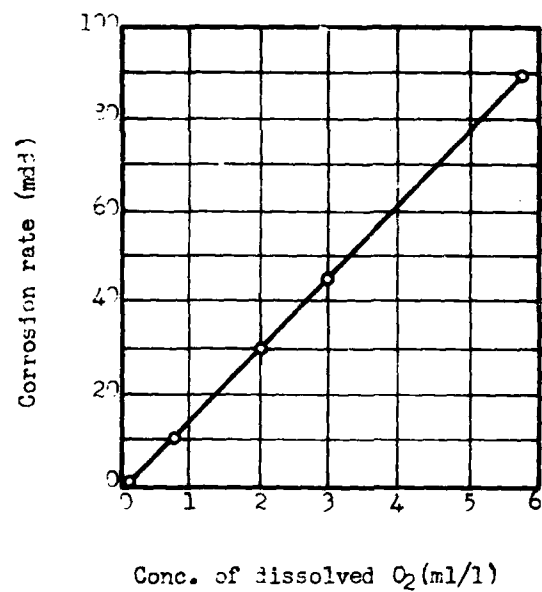


Figure 3. Effect of Dissolved Oxygen Concentration
on the Corrosion Rate of Steel¹⁹

Experimental Conditions: Water Containing
165 ppm CaCl_2 ; 48-Hour Test; 25°C.

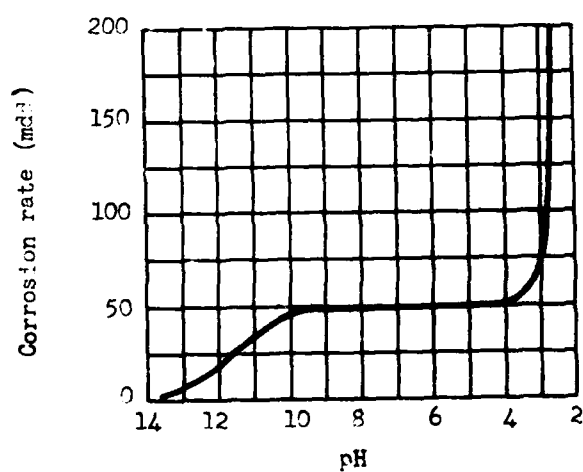


Figure 4. Effect of pH on the Corrosion Rate of Steel in Aerated Water at Room Temperature ²¹

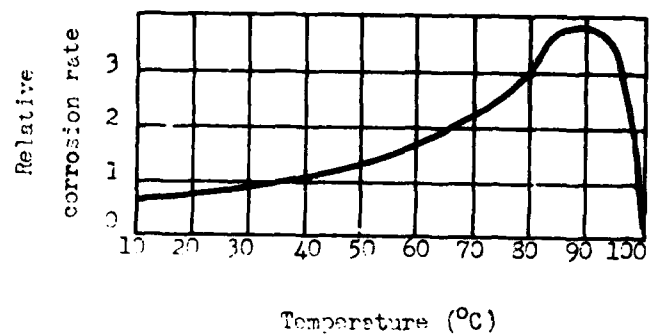


Figure 5. Effect of Temperature on the Corrosion Rate of Steel in Aerated Sea Water

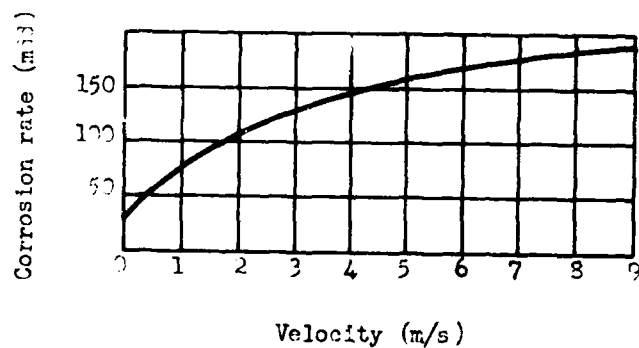


Figure 6. Effect of Velocity on the Corrosion Rate of Steel in Aerated Water at Atmospheric Temperature (composite of data, several investigations)

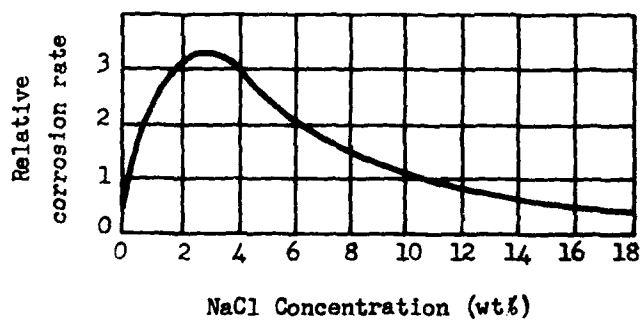


Figure 7. Effect of Salt Concentration on the Corrosion Rate of Steel in Aerated Solution at Room Temperature (composite of data, several investigations)

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